

# Non-Gaussian particle number fluctuations in vicinity of the critical point for van der Waals equation of state

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## Abstract

The non-Gaussian measures of the particle number fluctuations – skewness  $S\sigma$  and kurtosis  $\kappa\sigma^2$  – are calculated in a vicinity of the critical point. This point corresponds to the end point of the first-order liquid-gas phase transition. The gaseous phase is characterized by the positive values of skewness while the liquid phase has negative skew. The kurtosis appears to be significantly negative at the critical density and supercritical temperatures. The skewness and kurtosis diverge at the critical point. The classical van der Waals equation of state in the grand canonical ensemble formulation is used in our studies. Neglecting effects of the quantum statistics we succeed to obtain the analytical expressions for the rich structures of the skewness and kurtosis in a wide region around the critical point. These results have universal form, i.e., they do not depend on particular values of the van der Waals parameters  $a$  and  $b$ . The strongly intensive measures of particle number and energy fluctuations are also considered and show singular behavior in the vicinity of the critical point.

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## I. INTRODUCTION

The first-order phase transition is among the most general phenomena in physics. This phase transition exists in atomic and/or molecular systems, in the system of interacting nucleons (nuclear matter), and, most probably, in the QCD, between hadrons and quark-gluon plasma at large baryonic densities. The liquid-gas phase transition line in the plane of temperature  $T$  and chemical potential  $\mu$  has the end point, which is called the critical point (CP). The CP demonstrates some universal features typical for the second-order phase transitions, particularly, anomalously large fluctuations. The study of event-by-event fluctuations in high-energy nucleus-nucleus collisions opens new possibilities to investigate properties of strongly interacting matter (see, e.g., Refs. [1] and [2] and references therein) and the experimental search for the QCD CP is now in progress (see, e.g., Ref. [3] and references therein). The fluctuation signals of the QCD CP were discussed in Ref. [4], and higher moments of fluctuations of conserved charges were suggested as probes to study the phase structure of QCD [5, 6]. Particularly, the higher-order non-Gaussian measures such as the skewness  $S\sigma$  and kurtosis  $\kappa\sigma^2$  of conserved charges fluctuations have attracted much attention (see, e.g., Ref. [7] and [8]). Experimentally, the STAR collaboration has measured the higher moments of net-proton and net-charge multiplicity in Au+Au collisions [9–11]. See also recent review [12] on the search for critical behavior of strongly interacting matter at the CERN Super Proton Synchrotron. Calculations of higher moments of conserved charges has been performed in various effective QCD models [13–17]. The effects of non-equilibrium evolution of these observables in heavy-ion collisions have also been considered recently [18]. Another fluctuation measures of interest are the so-called strongly intensive quantities [19] which are normally not sensitive to the fluctuations of the system volume. This is especially relevant for heavy-ion collision experiments where size of the colliding system varies strongly on event-by-event level.

The van der Waals (VDW) equation is a simple analytical model of the pressure function  $p$  for equilibrium systems of particles with both attractive and repulsive interactions. In the canonical ensemble (CE) it reads as (see, e.g., Refs. [20, 21]),

$$p(T, n) = \frac{NT}{V - bN} - a\frac{N^2}{V^2} \equiv \frac{nT}{1 - bn} - an^2, \quad (1)$$

where  $n \equiv N/V$  is the particle number density while the VDW parameters  $a > 0$  and  $b > 0$

describe the attractive and repulsive interactions, respectively. The first term on the right-hand-side of Eq. (1) corresponds to the excluded volume (EV) correction, which manifests itself in a substitution of a total volume  $V$  by the available volume,  $V_{\text{av}} = V - bN$ . The second term comes from the mean field which describes attractive interactions between particles. With regards to its asymptotic behavior in the vicinity of the critical point the VDW model belongs to the mean-field theory universality class. The number of particles  $N$  is fixed in the CE. In order to apply the VDW equation of state to systems with variable number of particles and calculate their fluctuations the grand canonical ensemble (GCE) formulation is needed. This procedure was firstly performed for the EV model, i.e., for  $a = 0$  in Eq. (1), in Refs. [22, 23]. In our recent paper [24], the full VDW equation (1), with both attractive and repulsive terms, was transformed from the CE to the GCE for systems with Boltzmann statistics while the formulation which properly includes effects of quantum statistics was obtained in Ref. [25]. Note that the EV and VDW models can also be conveniently treated within the GCE in a framework of the thermodynamic mean-field approach (see Refs. [26–28]).

In the present paper we use our recent results of the GCE formulation [24] as a starting point for calculating the scaled variance, skewness, and kurtosis of particle number fluctuations, and also the strongly intensive measures of particle number and energy fluctuations. The Boltzmann approximation is adopted. This gives a possibility to obtain the analytical expressions for the universal structure of fluctuations in a vicinity of the CP.

The paper is organized as follows. In Sec. II the VDW equation of state is formulated within the GCE. In Sec. III the particle number fluctuations – scaled variance, skewness, and kurtosis – are calculated and their behavior in a vicinity of the CP is analyzed. In Sec. IV the strongly intensive measures of fluctuations for the energy and number of particles are considered. A summary in Sec. V closes the article.

## II. VDW EQUATION IN THE GCE

The canonical ensemble VDW pressure function in (1) corresponds to the Boltzmann approximation. This expression is used in the present paper, i.e., effects of the quantum statistics (Bose or Fermi) will be neglected. The VDW pressure is a unique function of variables  $T$  and

$n$  for all  $T \geq 0$  and  $0 \leq n \leq 1/b$ , and this equation of state contains the first-order liquid-gas phase transition and has the CP. The CP in  $(T, n)$ -plane, i.e. the point  $(T_c, n_c)$ , corresponds to the temperature and particle number density, where the following derivatives are equal to zero,

$$\left(\frac{\partial p}{\partial n}\right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial n^2}\right)_T = 0. \quad (2)$$

and the thermodynamical quantities at the CP are equal to:

$$T_c = \frac{8a}{27b}, \quad n_c = \frac{1}{3b}, \quad p_c = \frac{a}{27b^2}. \quad (3)$$

At  $T > T_c$  the following inequality is always valid,

$$\left(\frac{\partial p}{\partial n}\right)_T > 0, \quad (4)$$

while at  $T < T_c$  there appears an unstable interval  $[n_1, n_2]$  with

$$\left(\frac{\partial p}{\partial n}\right)_T < 0. \quad (5)$$

This means that the VDW isotherm  $p(T, n)$  has a local maximum at  $n = n_1$  and a local minimum at  $n = n_2 > n_1$  for  $T < T_c$ . The unstable part (5) of the VDW isotherm at the interval  $[n_1, n_2]$ , together with two additional metastable parts –  $[n_g, n_1]$  and  $[n_2, n_l]$  – are transformed to a mixture of two phases: a gas with density  $n_g < n_1$  and a liquid with density  $n_l > n_2$ . This is done in accordance with the Maxwell rule of the equal areas (see, e.g., Refs. [20, 21]) which leads to a constant pressure  $p(T, n_g) = p(T, n_l)$  inside the density interval  $[n_g, n_l]$ .

In the GCE the pressure should be defined in terms of its natural variables: temperature  $T$  and chemical potential  $\mu$ . The  $p(T, \mu)$  function contains a complete information about equilibrium physical systems. Other thermodynamical quantities, such as particle number density  $n(T, \mu)$ , entropy density  $s(T, \mu)$ , and energy density  $\varepsilon(T, \mu)$  can be presented in terms of  $p$  and its  $T$ - and  $\mu$ -derivatives:

$$n(T, \mu) = \left(\frac{\partial p}{\partial \mu}\right)_T, \quad s(T, \mu) = \left(\frac{\partial p}{\partial T}\right)_\mu, \quad \varepsilon(T, \mu) = T \left(\frac{\partial p}{\partial T}\right)_\mu + \mu \left(\frac{\partial p}{\partial \mu}\right)_T - p. \quad (6)$$

The VDW equation of state in the GCE is obtained in the form of transcendental equation for particle number density  $n \equiv n(T, \mu)$  as a function of  $T$  and  $\mu$  (see Ref. [24] for details):

$$n(T, \mu) = \frac{n^{\text{id}}(T, \mu^*)}{1 + b n^{\text{id}}(T, \mu^*)}, \quad \mu^* = \mu - T \frac{bn}{1 - bn} + 2an, \quad (7)$$

where  $n^{\text{id}}$  is a particle number density in the ideal Boltzmann gas

$$n^{\text{id}}(T, \mu) = \exp\left(\frac{\mu}{T}\right) \frac{d m^2 T}{2\pi^2} K_2\left(\frac{m}{T}\right) \quad (8)$$

with  $d$  being the degeneracy factor and  $m$  being the particle mass. The  $K_2(x)$  is the modified Bessel function of the second kind. The GCE VDW pressure  $p(T, \mu)$  is then obtained by inserting  $n(T, \mu)$  from (7) into Eq. (1). Note, the relativistic form of a dispersion relation is considered,  $\omega(k) = \sqrt{m^2 + k^2}$ , where  $\omega$  and  $k$  are the free single-particle energy and momentum, respectively<sup>1</sup>. This makes the present formulation being suitable for high-energy physics applications.

In the GCE there is a unique solution of Eq. (7) at  $T > T_c$ , while at  $T < T_c$  it may have either one solution or three different solutions for particle number density  $n(T, \mu)$ . In that case the solution which corresponds to a largest pressure survives in accordance to the Gibbs criterion. The liquid-gas mixed phase in the  $T$ - $\mu$  plane belongs to the line  $\mu = \mu_c(T)$ , where two solutions with different particle number densities,  $n_g(T, \mu)$  and  $n_l(T, \mu)$ , correspond to the equal pressures,  $p_g(T, \mu) = p_l(T, \mu)$ . The Maxwell rule of the equal areas and the Gibbs criteria of equal pressures for the gas and liquid at the same  $T$  and  $\mu$  values appear to be the equivalent descriptions of the first-order liquid-gas phase transitions (see Ref. [25] for details).

### III. PARTICLE NUMBER FLUCTUATIONS

#### A. Fluctuations in the GCE

Let the particle number  $N$  be a random variable with the normalized probability distribution  $\mathcal{P}(N)$ . The  $k$ -th moment  $\langle N^k \rangle$  is then defined as

$$\langle N^k \rangle = \sum_N N^k \mathcal{P}(N) . \quad (9)$$

Let us introduce the variance,  $\sigma^2 = \langle (\Delta N)^2 \rangle$ , where  $\Delta N \equiv N - \langle N \rangle$ . The scaled variance,

$$\omega[N] \equiv \frac{\sigma^2}{\langle N \rangle} , \quad (10)$$

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<sup>1</sup> We use the system of units, where the Plank constant  $\hbar$ , the speed of light  $c$ , and the Boltzmann constant  $k$  are equal to unity,  $\hbar = c = k = 1$ .

characterizes the width of the  $\mathcal{P}(N)$  distribution. Note that  $\omega[N] = 1$  for the Poisson distribution  $\mathcal{P}(N) = \exp(-\langle N \rangle) \langle N \rangle^N / N!$ .

The skewness  $S\sigma$  is defined as

$$S\sigma = \frac{\langle (\Delta N)^3 \rangle}{\sigma^2} . \quad (11)$$

The skewness measures the degree of asymmetry of the distribution  $\mathcal{P}(N)$  around its mean value  $\langle N \rangle$ . Positive skewness indicates a distribution with an asymmetric tail extending more to the *right*, i.e., toward  $N$ -values with  $N > \langle N \rangle$ . Negative skewness indicates a distribution with an asymmetric tail extending more to the *left*, i.e., toward  $N$ -values with  $N < \langle N \rangle$ . If the  $\mathcal{P}(N)$  distribution is symmetric around its mean value, i.e., the *right* and *left* tails are equal, it has zero skewness. This is the case for the normal Gaussian distribution, whereas the Poisson distribution shows a positive value of the skewness,  $S\sigma = 1$ .

The (excess) kurtosis  $\kappa\sigma^2$  is the measure of “peakedness” of the probability distribution  $\mathcal{P}(N)$ ,

$$\kappa\sigma^2 = \frac{\langle (\Delta N)^4 \rangle - 3 \langle (\Delta N)^2 \rangle^2}{\sigma^2} . \quad (12)$$

The kurtosis (12) measures the degree to which a distribution is more or less peaked than a normal Gaussian distribution. Positive kurtosis indicates a relatively peaked distribution. Negative kurtosis indicates a relatively flat distribution. For the Poisson distribution one has positive value of the kurtosis,  $\kappa\sigma^2 = 1$ .

The normal Gaussian distribution corresponds to the zero value of both the skewness (11) and the (excess) kurtosis (12). Therefore, (strong) deviations of  $S\sigma$  and/or  $\kappa\sigma^2$  from zero are the signatures of the (highly) non-Gaussian shape of the particle number distribution  $\mathcal{P}(N)$ .

In the GCE the system is defined by the pressure  $p$  given in terms of its natural variables  $T$  and  $\mu$ . The particle number fluctuations can be characterized by the following dimensionless cumulants (susceptibilities),

$$k_n = \frac{\partial^n (p/T^4)}{\partial (\mu/T)^n} , \quad (13)$$

which are connected to the moments of the particle number distribution as

$$k_1 = \frac{\langle N \rangle}{VT^3} , \quad k_2 = \frac{\langle (\Delta N)^2 \rangle}{VT^3} , \quad k_3 = \frac{\langle (\Delta N)^3 \rangle}{VT^3} , \quad k_4 = \frac{\langle (\Delta N)^4 \rangle - 3 \langle (\Delta N)^2 \rangle^2}{VT^3} , \quad (14)$$

where  $\langle \dots \rangle$  denotes the GCE averaging. The scaled variance (10), skewness (11), and kurtosis (12) are the intensive fluctuation measures that remain finite in the thermodynamic limit  $V \rightarrow \infty$ . They can be expressed in terms of the susceptibilities as the following

$$\omega[N] = \frac{k_2}{k_1}, \quad S\sigma = \frac{k_3}{k_2}, \quad \kappa\sigma^2 = \frac{k_4}{k_2}. \quad (15)$$

### B. Scaled variance

The scaled variance defined in Eq. (15) can be calculated through the  $\mu$ -derivative of the particle density. For pure phases in the classical VDW gas it results in (see also Ref. [24])

$$\omega[N] = \frac{T}{n} \left( \frac{\partial n}{\partial \mu} \right)_T = \left[ \frac{1}{(1 - bn)^2} - \frac{2an}{T} \right]^{-1}. \quad (16)$$

In terms of the reduced quantities,  $\tilde{T} \equiv T/T_c$  and  $\tilde{n} \equiv n/n_c$ , Eq.(16) reads as

$$\omega[N] = \frac{1}{9} \left[ \frac{1}{(3 - \tilde{n})^2} - \frac{\tilde{n}}{4\tilde{T}} \right]^{-1}, \quad (17)$$

and possesses the universal form independent of the specific values of the VDW parameters  $a$  and  $b$ . From Eq. (17) it follows that  $\omega[N] \rightarrow 1$  at  $\tilde{n} \rightarrow 0$  (this corresponds to the ideal gas limit and the Poisson  $\mathcal{P}(N)$  distribution), and  $\omega[N] \rightarrow 0$  at  $\tilde{n} \rightarrow 3$  (this corresponds to the liquid with the highest possible density). According to its definition, the scaled variance  $\omega[N]$  is a positive quantity. This is indeed the case for all  $T$  and  $n$  values that correspond to stable and even metastable states. The scaled variance diverges,  $\omega[N] \rightarrow \infty$ , at the CP. Introducing quantities  $\rho = \tilde{n} - 1$  and  $\tau = \tilde{T} - 1$  one finds at  $\tau \ll 1$  and  $\rho \ll 1$ :

$$\omega[N] \cong \frac{4}{9} \left[ \tau + \frac{3}{4}\rho^2 + \tau\rho \right]^{-1}. \quad (18)$$

The scaled variance (16) as a function of  $\tilde{T}$  and  $\tilde{n}$ , is plotted in Fig. 1 for both stable and metastable pure phases.

### C. Skewness

The skewness  $S\sigma$  can be calculated as

$$S\sigma = \frac{k_3}{k_2} = \omega[N] + \frac{T}{\omega[N]} \left( \frac{\partial \omega[N]}{\partial \mu} \right)_T = (\omega[N])^2 \left[ \frac{1 - 3bn}{(1 - bn)^3} \right]. \quad (19)$$

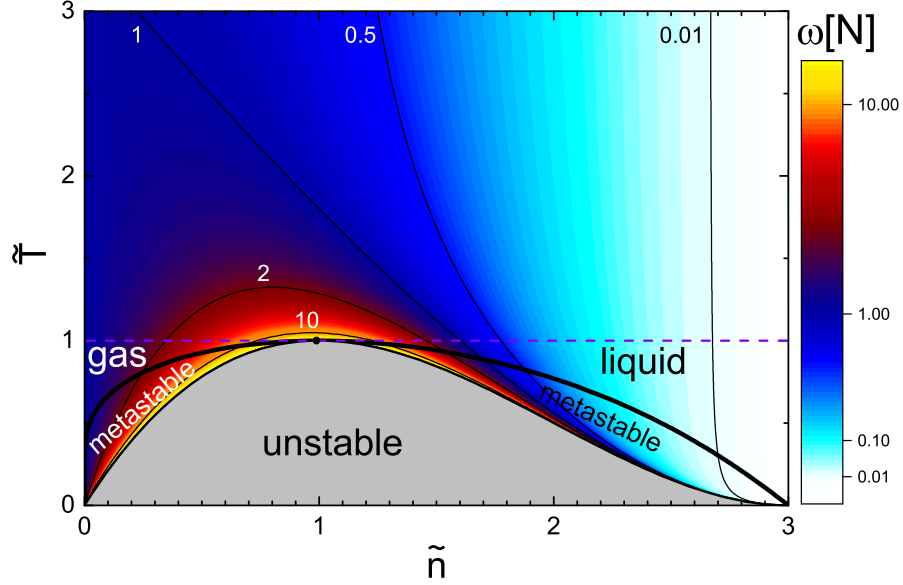


Figure 1: (Color online) The scaled variance  $\omega[N]$  (16) on the  $(\tilde{n}, \tilde{T})$  phase diagram for both stable and metastable pure phases. Several lines of constant values of  $\omega[N]$  are shown. The grey area depicts region where pure phase is mechanically unstable.

In the reduced variables it reads

$$S\sigma = \frac{1}{3} \left[ \frac{1}{(3 - \tilde{n})^2} - \frac{\tilde{n}}{4\tilde{T}} \right]^{-2} \left[ \frac{1 - \tilde{n}}{(3 - \tilde{n})^3} \right]. \quad (20)$$

As a function of the reduced temperature and density the skewness  $S\sigma$  is plotted in Fig. 2 for both stable and metastable pure phases. It is clearly seen from Eqs. (19) and (20) that the skewness is positive at  $\tilde{n} < 1$  (the gaseous phase), negative at  $\tilde{n} > 1$  (the liquid phase), and  $S\sigma = 0$  at  $\tilde{n} = 1$ . At  $\tilde{n} \rightarrow 0$  one finds that  $S\sigma \rightarrow 1$ . This is a small asymmetry of the particle number distribution and it corresponds to the Poisson distribution that takes place for the ideal Boltzmann gas.

In a vicinity of the CP one finds,

$$S\sigma \cong -\frac{2}{3}\rho \left[ \tau + \frac{3}{4}\rho^2 + \tau\rho \right]^{-2}. \quad (21)$$

The CP,  $\tilde{T} = \tilde{n} = 1$ , i.e.,  $\rho = \tau = 0$ , is a point of the essential singularity of the skewness measure. For example, at  $\tau = 0$  one finds from Eq. (21) that  $S\sigma \rightarrow +\infty$  at  $\rho \rightarrow +0$  and  $S\sigma \rightarrow -\infty$  at  $\rho \rightarrow -0$ . At the same time,  $S\sigma = 0$  at any  $\tau > 0$  and  $\rho = 0$ .



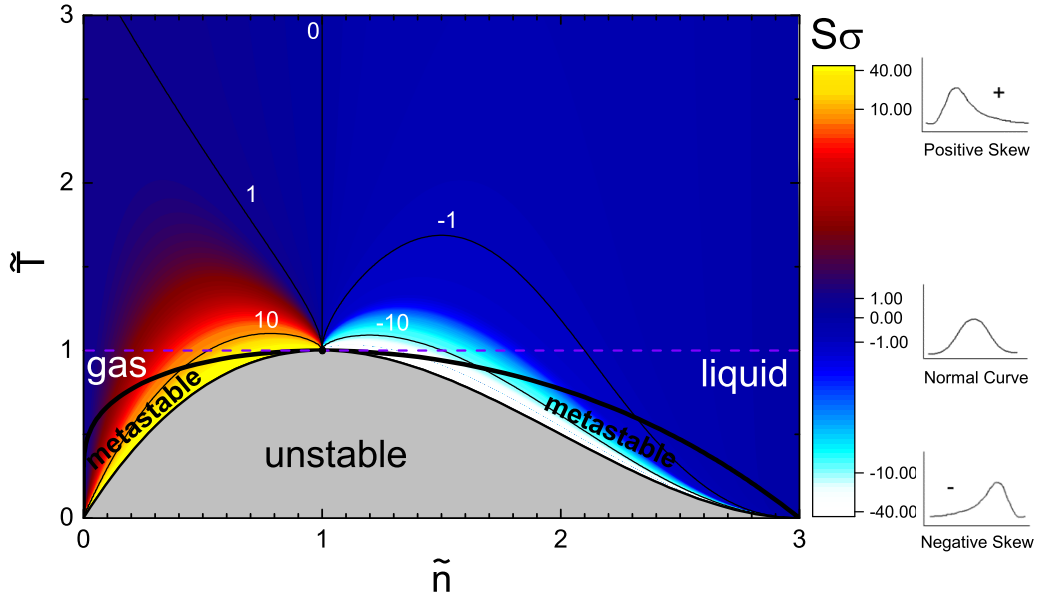


Figure 2: (Color online) The same as in Fig. 1 but for the skewness  $S\sigma$  (20). Different values of skewness are illustrated by the typical  $\mathcal{P}(N)$  distributions on the right panel.

### D. Kurtosis

The kurtosis  $\kappa\sigma^2$  can be calculated as

$$\kappa\sigma^2 = \frac{k_4}{k_2} = (S\sigma)^2 + T \left( \frac{\partial[S\sigma]}{\partial\mu} \right)_T = 3(S\sigma)^2 - 2\omega[N]S\sigma - 54(\omega[N])^3 \frac{\tilde{n}^2}{(3-\tilde{n})^4}. \quad (22)$$

As a function of the reduced temperature and density the kurtosis  $\kappa\sigma^2$  is plotted in Fig. 3 for both stable and metastable pure phases. It is seen from these figures that at  $\tilde{T} < 1$  the kurtosis is positive (leptokurtic) for both  $\tilde{n} < 1$  (the gaseous phase) and  $\tilde{n} > 1$  (the liquid phases).

Approaching the CP the kurtosis diverges. At  $\tau = 0$  and  $\rho \ll 1$  one finds

$$\kappa\sigma^2 \propto \rho^{-6} . \quad (23)$$

Notably, the kurtosis has attains large negative values (platykurtic) at critical density  $\tilde{n} = 1$  and temperatures just above the critical,  $\tilde{T} > 1$ . In this region, one finds

$$\kappa\sigma^2 \propto -\tau^{-3}. \quad (24)$$

This indicates that particle number distribution has a flat peak in that region, much flatter than the corresponding Gaussian with the same width. This region can be identified as the crossover

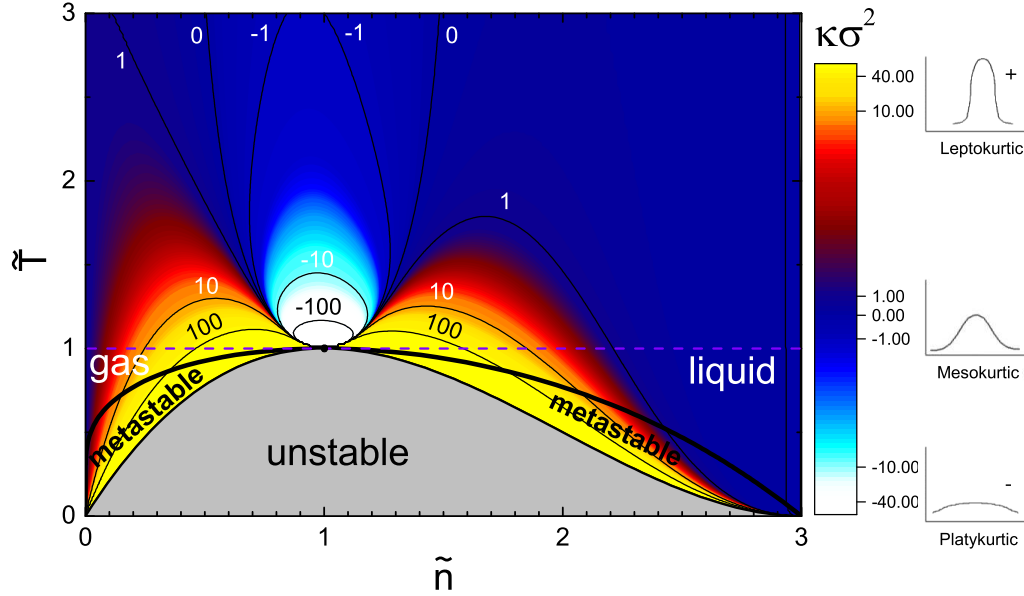


Figure 3: (Color online) The same as in Figs. 1 and 2 but for the kurtosis  $\kappa\sigma^2$  (22). Different values of kurtosis are illustrated by the typical  $\mathcal{P}(N)$  distributions on the right panel.

region, where rapid although smooth transition between gaseous and liquid phases takes place. This is in line with arguments that the crossover region near the CP is characterized by the negative sign of kurtosis [8]. In the vicinity of the CP the kurtosis changes rapidly and attains both positive and negative values.

At  $\tilde{n} \rightarrow 0$  the VDW equation of state corresponds to the ideal Boltzmann gas limit. In this case,  $\mathcal{P}(N)$  approaches the Poisson distribution, and, as it follows from Eqs. (20) and (22), the skewness and kurtosis both approach the Poisson expectation values, i.e.,  $S\sigma \rightarrow 1$  and  $\kappa\sigma^2 \rightarrow 1$ . It should be noted that the ideal Boltzmann gas with the Poisson distribution reveals small deviations from the Gaussian  $\mathcal{P}(N)$  distribution for which, by construction,  $S\sigma = 0$  and  $\kappa\sigma^2 = 0$ .

The nucleon number fluctuations were recently considered in Ref. [29] within the modified VDW equation. To describe the nuclear matter ground state the Fermi statistics of nucleons was introduced [25]. The Boltzmann approximation is assumed in the present study and it corresponds to the original version of the VDW equation. This gives a possibility to obtain the analytical expressions for the scaled variance, skewness, and kurtosis. Note also that our results for the particle number fluctuations presented in Figs. 1-3 are universal, i.e., they are

independent on the specific numerical values of the VDW parameters  $a$  and  $b$ . Therefore, they can be applied to very different physical systems – from the CP of water with  $T_c = 647 \text{ K}$  up to the CP in of the nuclear matter with  $T_c \cong 2 \times 10^{12} \text{ K}$ . The universality of the results is lost if one would take into account the effects of quantum statistics. On the other hand, in most cases the inclusion of Fermi statistics changes the results on a quantitative level, qualitatively they remain essentially the same as in case of the Boltzmann statistics.

#### IV. STRONGLY INTENSIVE QUANTITIES

The results of the previous section demonstrate a strong increase of the particle number fluctuations in a vicinity of the CP. The fluctuations may become also very large for metastable states, i.e., super-cooled gas and/or super-heated liquid. These fluctuation signals from phase transitions in the nuclear matter can be observed in the event-by-event analysis of heavy ion collisions. Note, however, that in these processes there is one more source of particle number fluctuations, namely, event-by-event fluctuations of the system volume. These volume fluctuations are mainly of the geometrical origin, and they can hardly be avoided in nucleus-nucleus reactions. Thus, one may observe large experimental fluctuations even for simple statistical systems, e.g., the ideal gas. The strongly intensive measures of the fluctuations defined in terms of two extensive quantities  $A$  and  $B$  were suggested in Ref. [19]. For statistical systems in a case of the absence of phase transitions these measures within the GCE formulation are independent of the system volume and its fluctuations. Note, however, that in systems with the CP (in general, for the 2nd order phase transitions) the critical behavior does depend on the system volume and shows the characteristic finite-size scaling. This implies that strongly intensive quantities are also volume-dependent near the CP. Thus, using the strongly intensive measures one excludes trivial volume fluctuations for normal statistical systems, and a presence of large fluctuations in terms of these measures can be considered as an indication of critical behavior.

In the present paper we consider the strongly intensive measures of total energy  $E$  and

particle number  $N$  fluctuations for the VDW equation of state. They are defined as

$$\Delta[E, N] = C_{\Delta}^{-1} \left[ \langle N \rangle \omega[E] - \langle E \rangle \omega[N] \right], \quad (25)$$

$$\Sigma[E, N] = C_{\Sigma}^{-1} \left[ \langle N \rangle \omega[E] + \langle E \rangle \omega[N] - 2 \left( \langle EN \rangle - \langle E \rangle \langle N \rangle \right) \right], \quad (26)$$

where  $C_{\Delta}^{-1}$  and  $C_{\Sigma}^{-1}$  are the normalization factors that have been suggested in the following form [30]

$$C_{\Delta} = C_{\Sigma} = \langle N \rangle \omega[\varepsilon], \quad (27)$$

with  $\omega[\varepsilon]$  being the scaled variance of a single-particle energy distribution in the VDW system. To proceed it is necessary to calculate  $\omega[\varepsilon]$ ,  $\omega[E]$ , and  $\langle EN \rangle$ .

In the VDW gas the average single-particle energy  $\bar{\varepsilon}$  is independent of the parameter  $b$ , but it is modified due to a presence of the attractive mean field:

$$\bar{\varepsilon} = \bar{\varepsilon}_{\text{id}}(T) - a \frac{N}{V} = 3T + m \frac{K_1(m/T)}{K_2(m/T)} - an, \quad (28)$$

where  $\bar{\varepsilon}_{\text{id}}$  is the average single-particle energy in the relativistic ideal gas. The variance of the single-particle energy is insensitive to the presence of the VDW mean field, and one obtains

$$\omega[\varepsilon] = \frac{\overline{\varepsilon^2} - \bar{\varepsilon}^2}{\bar{\varepsilon}} = \frac{T^2}{\bar{\varepsilon}} \frac{\partial \bar{\varepsilon}_{\text{id}}}{\partial T}. \quad (29)$$

The mean total energy is

$$\langle E \rangle = \left\langle \left( \bar{\varepsilon}_{\text{id}} - a \frac{N}{V} \right) N \right\rangle = \bar{\varepsilon}_{\text{id}} \langle N \rangle - \frac{a}{V} \langle N^2 \rangle = \bar{\varepsilon}_{\text{id}} \langle N \rangle - \frac{a}{V} \langle N \rangle^2 - a \frac{\langle N^2 \rangle - \langle N \rangle^2}{V}. \quad (30)$$

The first and second terms in the right hand side of Eq. (30) are proportional to  $\langle N \rangle$ . On the other hand, the third term remains finite outside the critical point in the thermodynamic limit  $V \rightarrow \infty$ . Therefore, one obtains

$$\langle E \rangle \cong (\bar{\varepsilon}_{\text{id}} - an) \langle N \rangle. \quad (31)$$

For  $\omega[E]$  one then finds

$$\omega[E] \equiv \frac{\langle E^2 \rangle - \langle E \rangle^2}{\langle E \rangle} = \frac{1}{\langle E \rangle} T^2 \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{\mu/T} = \omega[\varepsilon] + \frac{(\bar{\varepsilon}_{\text{id}} - 2an)^2}{\bar{\varepsilon}_{\text{id}} - an} \omega[N]. \quad (32)$$

Finally, the correlations between  $E$  and  $N$  can be calculated as the following

$$\langle EN \rangle - \langle E \rangle \langle N \rangle = T^2 \left( \frac{\partial \langle N \rangle}{\partial T} \right)_{\mu/T} = (\bar{\epsilon}_{\text{id}} - 2an) \langle N \rangle \omega[N]. \quad (33)$$

Substituting the above formulae into Eqs. (25) and (26) one finds the following expressions for the strongly intensive quantities:

$$\Delta[E, N] = 1 - \frac{an(2\bar{\epsilon}_{\text{id}} - 3an)}{\bar{\epsilon}_{\text{id}}^2 - \bar{\epsilon}_{\text{id}}^2} \omega[N], \quad (34)$$

$$\Sigma[E, N] = 1 + \frac{a^2 n^2}{\bar{\epsilon}_{\text{id}}^2 - \bar{\epsilon}_{\text{id}}^2} \omega[N]. \quad (35)$$

In the absence of the attractive interactions (i.e.,  $a = 0$ ), one can readily see from Eqs. (34) and (35) that  $\Delta[E, N] = \Sigma[E, N] = 1$ , thus, in the excluded-volume model the strongly intensive quantities are the same as in the ideal Boltzmann gas.

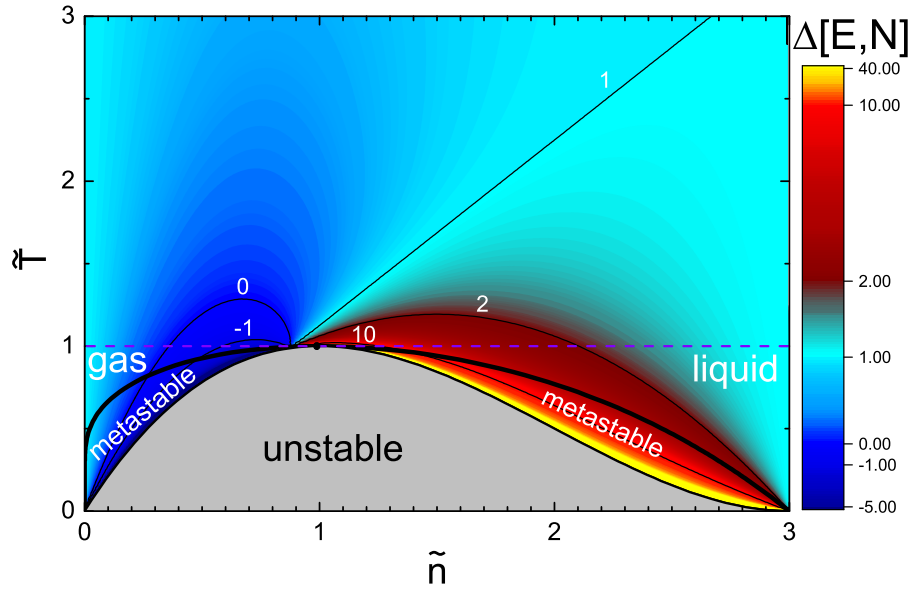


Figure 4: (Color online) The strongly intensive quantity  $\Delta[E, N]$  (36) on the  $(\tilde{n}, \tilde{T})$  phase diagram for both stable and metastable pure phases. Several lines of constant values of  $\Delta[E, N]$  are shown.

The expressions (34) and (35) for  $\Delta[E, N]$  and  $\Sigma[E, N]$  become more transparent if one considers the non-relativistic limit,  $\bar{\epsilon}_{\text{id}} = 3T/2$  and  $\bar{\epsilon}_{\text{id}}^2 - \bar{\epsilon}_{\text{id}}^2 = 3T^2/2$ . Note that the rest energy,  $m$ , has been subtracted, thus, only the kinetic energy fluctuations contribute to  $\bar{\epsilon}_{\text{id}}^2$ . One then

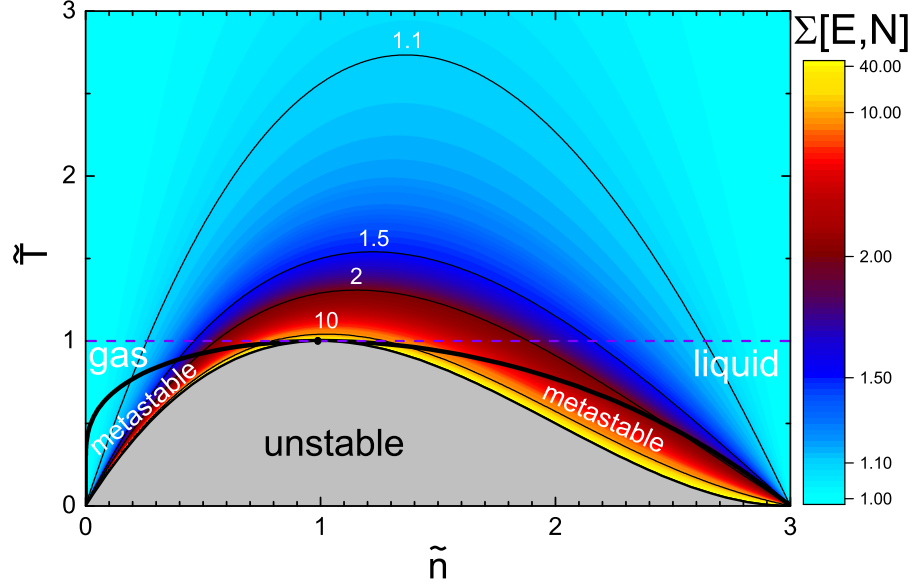


Figure 5: (Color online) The strongly intensive quantity  $\Sigma[E, N]$  (37) on the  $(\tilde{n}, \tilde{T})$  phase diagram for both stable and metastable pure phases. Several lines of constant values of  $\Sigma[E, N]$  are shown.

obtains

$$\Delta[E, N] = 1 - \frac{2}{3} \frac{an(3T - 3an)}{T^2} \omega[N] = 1 - \frac{9\tilde{n}}{4\tilde{T}} \left[ 1 - \frac{9\tilde{n}}{8\tilde{T}} \right] \omega[N], \quad (36)$$

$$\Sigma[E, N] = 1 + \frac{2}{3} \frac{a^2 n^2}{T^2} \omega[N] = 1 + \frac{27}{32} \frac{\tilde{n}^2}{\tilde{T}^2} \omega[N]. \quad (37)$$

The quantities  $\Delta[E, N]$  and  $\Sigma[E, N]$  are depicted in Figs. 4 and 5, respectively. Both the  $\Sigma[E, N]$  and  $\Delta[E, N]$  measures approach unity in both zero density,  $\tilde{n} \rightarrow 0$ , and packing,  $\tilde{n} \rightarrow 3$ , limits and diverge at the CP. Note that the  $\Sigma[E, N]$  measure is always positive and even larger than unity, while the  $\Delta[E, N]$  measure attains both positive and negative values.

## V. SUMMARY

Particle number fluctuations up to the fourth order – scaled variance  $\omega[N]$ , skewness  $S\sigma$ , and kurtosis  $\kappa\sigma^2$  – have been calculated for the classical van der Waals equation of state. Analytical formulae were obtained and used for an analysis of the fluctuation behavior in a vicinity of the CP. The obtained results have the universal form, i.e., they are independent of the specific numerical values of the VDW parameters  $a$  and  $b$ .

The skewness  $S\sigma$  is positive at  $n < n_c$  and negative at  $n > n_c$  for all values of temperature. This means that gaseous and liquid phases at  $T < T_c$  are clearly characterized by positive and negative values of  $S\sigma$ , respectively. Above the critical temperature  $T_c$  the skewness is equal to zero at the  $n = n_c$  line, and this line can be associated with the crossover transition from gaseous to liquid matter.

The kurtosis  $\kappa\sigma^2$  is very sensitive to the proximity of the critical point and also has a rich structure. At  $T < T_c$  the kurtosis is positive in both phases. In the vicinity of the CP the kurtosis changes rapidly and can attain both positive and negative values at  $T > T_c$ . Notably, in the crossover region just above  $T_c$  it attains large negative values.

The strongly intensive measures  $\Delta[E, N]$  and  $\Sigma[E, N]$  for the fluctuations of system energy and number of particles have been also calculated. In the excluded-volume model, i.e. at  $a = 0$ , these measures are the same as in the ideal gas and are equal to unity. In the full van der Waals equation, however, they diverge at the critical point and differ significantly from unity in the region around it. These measures can be used to study the fluctuations in the nuclear matter created in heavy ion collisions.

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